Raman spectroscopic study kuranakhite $PbMn^{4+}Te^{6+}O_6$ –a rare tellurate mineral

Ray L. Frost • and Eloise C. Keeffe

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

Tellurates are rare minerals as the tellurate anion is easily reduced to the tellurite ion. An example of a tellurate containing mineral is kuranakhite. Two bands at 617 and 686 cm^{-1} are observed and assigned to the $Te^{6+}O_6$ ν_1 symmetric stretching mode. The observation of two bands suggests the non-equivalence of the $Te^{6+}O_6$ in the structure. The broad band centred at 743 cm^{-1} is attributed to the $Te^{6+}O_6$ ν_3 antisymmetric stretching mode. Sharp intense bands at 452 and 462 cm^{-1} are assigned to the $Te^{6+}O_6$ ν_4 bending mode. A comparion of the Raman spectra of kuranakhite with that of tellurate containing minerals tlapallite and xocomecatlite is made.

KEYWORDS: tellurate, kuranakhite, xocomecatlite, tlapallite, Raman spectroscopy,

INTRODUCTION

There exists in nature, a collection of minerals based upon the elements selenium and tellurium. These minerals are the tellurates/selenates and the tellurites/selenites. They minerals may be subdivided into groups according to formula and structure [1]. There are five groups based upon the formulae (a) $A(XO_3)$, (b) $A(XO_3)\cdot xH_2O$, (c) $A_2(XO_3)_3\cdot xH_2O$, (d) $A_2(X_2O_5)$ and (e) $A(X_3O_8)$. Of the selenites, molybdomenite is an example of type (a); chalcomenite, clinochalcomenite, cobaltomenite and ahlfeldite are examples of type (b) mandarinoite is an example of type (c). There are no known examples of selenite minerals with formulae (d) and

• Author to whom correspondence should be addressed (r.frost@qut.edu.au)

(e). The tellurite group, however, consists of minerals that can be categorised into each of the five formula types.

Tellurates are very rare minerals because the tellurate anion is very easily reduced to the tellurite anion. There are three types of tellurate minerals: type (a) $(AB)_m(TeO_4)_pZ_q$, type (b) $(AB)_m(TeO_6)\cdot xH_2O$ and type (c), compound tellurates in which a second anion is involved. An example of type (a) is the mineral xocomecatlite [2-4]. Kuranakhite is also an example from this group. Xocomecatlite, $Cu_3TeO_4(OH)_4$, is related to the mineral tlalocite, $Cu_{10}Zn_6(TeO_3)(TeO_4)_2Cl(OH)_{25}\cdot 27H_2O$. Both originate from Moctezuma, Sonora, Mexico. Another related tellurate mineral is tlapallite $H_6(Ca,Pb)_2(Cu,Zn)_3SO_4(TeO_3)_4TeO_6$ which is a mixed anionic mineral containing both tellurate and tellurite anions.

In contrast to the extensive list of tellurites, there are very few tellurate minerals. The tellurate ion can be either TeO_4^{2-} or TeO_6^{6-}. Unlike sulphate, tellurate is a good oxidizing agent; it can be reduced to tellurite or tellurium. The E^0 value is significant as it gives an indication of the strength of the tellurate ion as an oxidising agent.

$$TeO_4^{2-} \rightarrow TeO_3^{2-} + 1/2O_2 \quad (E^0 = -1.042V)$$

Tellurate exists in two forms, metatellurate ion, TeO_4^{2-}, and orthotellurate ion, TeO_6^{6-}. Compounds include both metatellurates and orthotellurates. Metatellurates are analogous to sulfates, however, they are rare. Orthotellurates are much more common and therefore forms most of the chemistry of tellurates. In neutral conditions, pentahydrogen orthotellurate ion, $H_5TeO_6^-$, is most common; in basic conditions, tetrahydrogen orthotellurate ion, $H_4TeO_6^{2-}$, is most common and in acid conditions, the orthotelluric acid, H_6TeO_6, is more common. The number of tellurate minerals is greatly overshadowed by the number of tellurites minerals, minerals containing TeO_3^{2-} units.

Raman spectroscopy has proven most useful for the study of minerals especially where X-ray crystallographic data is uncertain or unknown. [5-15] Diagenetically related minerals such as tellurates and tellurites may be studied using

Raman spectroscopy [16-21]. The tellurite ion is a strong oxidising agent and thus it is rare to find a mineral with the tellurate ion and not have the tellurite or some other anion present. The objective of this paper is to present the Raman spectrum of kuranakhite and to relate the spectra to the molecular structure of the mineral.

EXPERIMENTAL

Minerals

The mineral kuranakhite was sourced from kuranakh depsoit, Russia. This is the „type' mineral. The composition of the mineral, obtained from different sources, has been reported by Anthony *et al.* (page 377) [22]. The analysis of the mineral was TeO_3 36.2%, MnO_2 17.9% and PbO 46.0%. This provides a formula for the mineral as $Pb_{0.93}Mn_{0.81}TeO_6$. The single crystal X-ray study of the mineral has not been undertaken. Powder XRD indicates the mineral is orthorhombic. [23]

Raman microprobe spectroscopy

Crystals of the kuranakhite were placed and orientated on the stage of an Olympus BHSM microscope which was equipped with 10x and 50x objectives as part of a Renishaw 1000 Raman microscope system. The system also includes a monochromator, filter system and Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a nominal resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}.

Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Gauss-Lorentz, cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations (r^2)

greater than 0.995.

RESULTS AND DISCUSSION

Farmer [24] states that very little research has been undertaken on the vibrational spectroscopy of tellurates. As such very few papers have been forthcoming. Only a few minerals with the tellurate anion have been discovered [2-4]. The metatellurate anion TeO_4^{2-} should have T_d symmetry and therefore four internal modes, namely A_1 (ν_1), E (ν_2) and $2F_2$ (ν_3 and ν_4) . The orthotellurate ion, TeO_6^{6-} will have octahedral symmetry but may be strongly distorted. Vibrational modes for the tellurate anion should occur in the 620 to 650 cm^{-1} region and in the 290 to 360 cm^{-1} region. If the symmetry of the tellurate anion is reduced through for example bonding to a cation as in the kuranakhite structure then the loss of degeneracy will occur, and additional bands observed. Siebert [25] reported the infrared spectra of selected synthetic tellurates and antimonates. The position of the bands for the TeO_6^{6-} anion was defined by Siebert as ν_1 650 cm^{-1} (A_{1g}), ν_3 630 cm^{-1} (E_g), ν_2 375 cm^{-1} (F_{2g}). For the compound H_6TeO_6 infrared bands were observed at 605, 650, 658, 675, 708 and 730 cm^{-1} and were assigned to TeO stretching vibrations. In addition an intense band at 411 cm^{-1} is assigned to a δTeO bending mode (presumably ν_4 vibration). For the compound $Na_2H_4TeO_6$ infrared bands were observed at 429, 536, 587, 675 and 780 cm^{-1}. More complexity was observed in the spectrum of $K_2H_4TeO_6{\cdot}3H_2O$. Siebert also provided data for the compound $(H_4TeO_4)_x$. For this polytellurous acid, infrared bands were found at 450 cm^{-1} (δTeO) and stretching modes at 600, 720, 800 cm^{-1}. According to Siebert the TeO_6^{6-} anion is octahedral but is distorted. Thus infrared forbidden bands are activated.

The Raman spectrum of kuranakhite $PbMn^{4+}Te^{6+}O_6$ in the 100 to 900 cm^{-1} region is dispalyed in Fig. 1. Two bands at 617 and 686 cm^{-1} are observed and assigned to the $Te^{6+}O_6$ ν_1 symmetric stretching mode. The observation of two bands suggests the non equivalence of the $Te^{6+}O_6$ in the structure. Such a concept would need to be confirmed by X-ray diffraction. The broad band centred at 743 cm^{-1} is attributed to the $Te^{6+}O_6$ ν_3 antisymmetric stretching mode. The width of this band may indicate that it is composed of a number of overlapping bands. The assignment of the

$Te^{6+}O_6$ stretching bands is at variance to that proposed by Siebert. [25] The sharp intense band at 462 cm^{-1} is assigned to the $Te^{6+}O_6$ ν_4 bending mode. A second overlapping band at 452 cm^{-1} assigned to the same vibrational mode. The observation of two ν_4 bending modes fits well with the concept of two non-equivalent $Te^{6+}O_6$ units in the mineral structure. The band at 407 cm^{-1} may be assigned to the ν_2 bending mode. The position of this band appears high compared with the data of Siebert.

A comparison may be made with the Raman spectra of other tellurate minerals. In the Raman spectrum of xocomecatlite $Cu_3(OH)_4TeO_4{\cdot}H_2O$ (Fig. 2) a broad band that may be decomposed into component bands at 710, 763 and 796 cm^{-1}. Thee bands are quite sharp. One possible assignment is the band at 796 cm^{-1} is ascribed to the TeO_4 ν_1 symmetric stretching mode and the two bands at 710 and 763 cm^{-1} to the TeO_4 antisymmetric stretching mode. Another tellurate containing mineral which may be useful for a comparison of the Raman spectra of kuranakhite is the mixed anionic mineral tlapallite $H_6(Ca,Pb)_2(Cu,Zn)_3SO_4(TeO_3)_4TeO_6$. This mineral contains both the tellurite and tellurate anions in the structure. Raman bands are observed for tlapallite at 650, 708, 764 and 796 cm^{-1} (Fig. 3). It is difficult to nominate a specific assignment for each of these bands, as the tellurate and tellurite bands overlap. One probable assignment is as follows: the higher wavenumber bands may be attributed to the tellurate ion $(TeO_6)^{2-}$ and the lower wavenumber bands to the tellurite anion $(TeO_3)^{2-}$. Thus, the Raman band at 796 cm^{-1} is attributed to the ν_1 $(TeO_6)^{2-}$ antisymmetric stretching mode and the band at 764 cm^{-1} to the ν_1 $(TeO_3)^{2-}$ symmetric stretching mode. The band at 708 cm^{-1} may be attributed to the ν_1 $(TeO_6)^{2-}$ symmetric stretching mode and the band at 691 cm^{-1} to the ν_1 $(TeO_3)^{2-}$ antisymmetric stretching mode. Importantly Raman bands are observed in similar positions for these three tellurate containing minerals.

CONCLUSIONS

In nature, very few tellurate minerals exist. They may be subdivided according to formula and structure. The tellurate ion is TeO_4^{2-} or TeO_6^{6-}. Unlike sulphate, tellurate is a good oxidizing agent; it can be reduced to tellurite or even tellurium. As a result of this, the number of tellurite minerals greatly out numbers that of tellurate minerals. The ready reduction of the tellurate anion to the tellurite anion leads to

certain minerals such as tlapallite forming mixed anionic species in which both the tellurate and tellurite ions exist. The mineral kuranakhite is one in which the tellurate anion TeO_6^{6-} is retained. Raman spectroscopy has been used to characterise the molecular structure of kuranakhite.

Acknowledgements

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224 **List of Figs**

225

226 Fig. 1 Raman spectrum of kuranakhite in the 100 to 900 cm^{-1} region.

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228 Fig. 2 Raman spectrum of xocomecatlite in the 550 to 900 cm^{-1} region.

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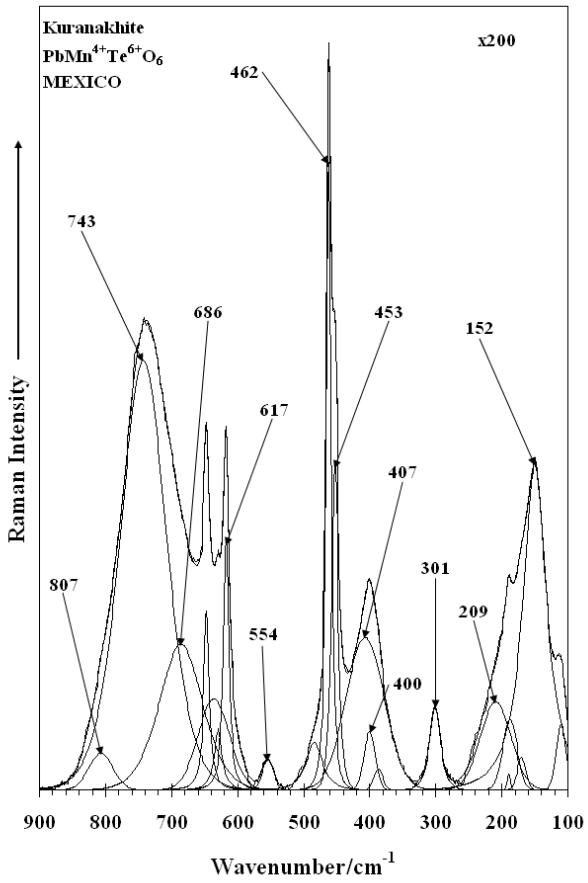
230 Fig. 3 Raman spectrum of tlapallite in the 600 to 900 cm^{-1} region.



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232

233 **Fig. 1**

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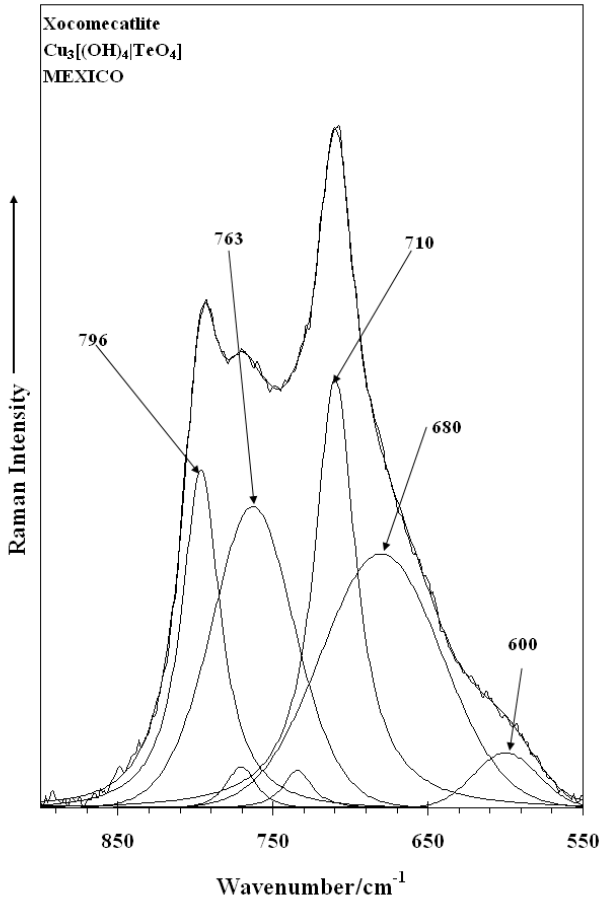

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237 **Fig. 2**

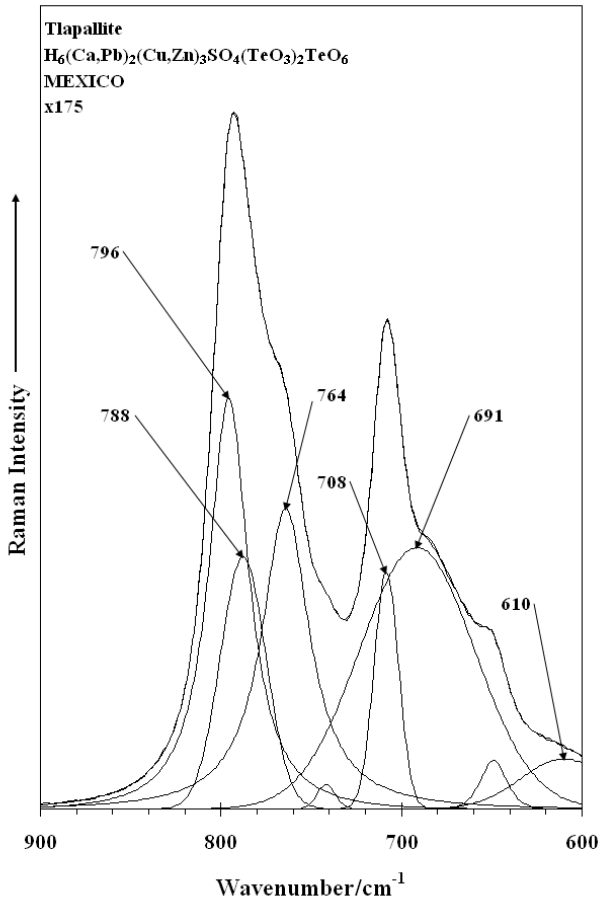
Tlapallite
H6(Ca,Pb)2(Cu,Zn)3SO4(TeO3)2TeO6
MEXICO
x175
796
788
764
708
691
610
Raman Intensity
900
800
700
600
Wavenumber/cm-1

Fig. 3